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Development of GaN-based Nanostructure Photon Emitters

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Principal Investigator

Professor S. C. Wang

Institution

Institute of Electro-Optical Engineering,
National Chiao Tung University
1001 Ta Hsueh Road, Hsinchu, TAIWAN 30010
Phone: +886-3-5712121 extension 56320
Fax: +886-3-5716631
Email: scwang@mail.nctu.edu.tw

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14. ABSTRACT
This is the report of research to develop and establish a viable new epitaxial growth technique with better thickness control, low defect density, and high quality epitaxial film for use in growth of photonic emitters.

15. SUBJECT TERMS
Laser Physics, Quantum Dots, Materials Preparation

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1. Background

GaN-based wide bandgap semiconductors are very important material system for fabrication of photon emitters in a wide range of wavelength. In particular the light emitters in ultraviolet (UV), blue and green wavelength have been developed and demonstrated in recent years. Besides these UV and visible light emitters, the unique properties of GaN material system such as large exciton energy and large LO phonon energy have been proposed as a very suitable material candidate for realization of various photon emitters such single photon emitter, LED, vertical cavity surface emitting laser (VCSEL) and quantum cascade laser (QCL) at room temperature. During the past several years our research group at National Chiao Tung University (NCTU) under the support of our National Nano Science and Technology Program Office of National Science Council (NSC) has been engaged in the research and development of GaN-based quantum confined structures and nanostructures for control of photon emission, and has successfully developed and demonstrated various blue and UV emitters including the high efficiency blue light emitter diodes(LEDs) and blue vertical cavity surface emitting lasers(VCSELs). In addition our research group has also been engaged the development of GaN-based quantum cascade device for generation of THz emission in the recent years under the sponsorship of U. S. AFOSR. We have collaborated with Dr. Richard Soref of AFRL at Hanscom and Prof. Greg Sun of U of Mass Boston in this initial research effort.

All these GaN-based photon emitting devices are mostly grown on the foreign substrate such as sapphire which has large lattice mismatched wit GaN. As a result there are defects in the grown nanostructures such as multiple quantum well (MQW) structure for devices such as QCL, LED, and VCSEL when the structures are grown by conventional MOCVD epitaxial growth method. In this proposed work we will develop a new epitaxial grown approach to reduce the defect density, improve epilayer quality and achieve better thickness control by using atomic layer deposition technique for grow MQW and various nanostructures for application to QCL,LED and VCSEL. This effort was conducted in collaboration with Dr. Richard Soref of AFRL at Hanscom and Prof. Greg Sun of U of Mass Boston.

2. Scientific Objective

The main objective of this effort has twofold: one is to continue our previous research effort to develop and establish a viable new epitaxial growth technique with better thickness control, low defect density and high quality epitaxial film for use in growth of photonic emitters. Second is to investigate and characterize the grown MQW active layer structures and to verify the improved performance of the device grown by the improved growth technique. The precision control of epitaxial layer thickness and composition are critical to GaN-based Photon emitter device performance; while the understanding of the optical characteristics and structural properties of the grown structures are important for refinement and optimization of device design and growth techniques for fabrication of a functional photon emitting devices.

2 Technical approach and accomplishment

2.1 Description of Atomic Layer Deposition (ALD) technique

The ALD process involves alternate control of mass flow of TMAl and TMGa gas during the growth of AlGaN barrier to form six pairs of AlN/GaN SLs. The TMAl and TMGa flow time of AlN and GaN layer were 6.8 and 19.8 sec, respectively under a continuous flow of the NH_3 gas at 850°C. The interruption time was 10 sec between AlN and GaN alternating layers. The growth rate of ALD AlGaN barrier was measured by an *in-situ* optical monitoring system, Filmetrics, and the growth rate was 0.14 µm/hr which was lower than the conventional growth rate of about 0.6 ~ 1 µm/hr. After AlGaN barrier was grown, only TMGa was introduced into the reactor for 34.8 second to grow the GaN well. Fig. 1 shows the growth procedure of AlGaN barrier and GaN well layers

2.2 Fabrication of AlGaN/GaN MQW

The AlGaN/GaN MQW structures were grown by the low-pressure metal-organic chemical vapor deposition VEECO D75 system. The TMGa, TMAl and gaseous NH_3 were employed as the reactant sources for Ga, Al and N, respectively and H_2 and N_2 were used as the carrier gaseous. The (0001)-oriented sapphire substrate with a 0.2° offset was first heated to 1000°C under an H_2 ambient for 5 min. Then, a 2-µm-thick GaN epilayer was grown after the deposition of a low-temperature nucleation layer. Finally, the AlGaN/GaN MQWs structure comprising three GaN wells and four AlGaN barriers were grown at 850°C in H_2+N_2 atmosphere. Particularly, the AlGaN barriers were grown using the ALD technique.

2.3 Characterization of AlGaN/GaN MQW with ALD grown barrier

The surface morphology of the as-grown sample was observed by atomic force microscope (AFM) with a scanning area of 5 µm × 5 µm. Crystalline quality was evaluated by high resolution X-ray diffraction (HRXRD) and reciprocal space mapping (RSM), and Cu K_α radiation was used as the X-ray source. The average thicknesses of the AlGaN barriers and the GaN wells were determined from the angular distance between satellite peaks in (0002) ω/2θ-scan. The optical properties were investigated by PL measurements. PL spectra were excited with a frequency tripled Ti: sapphire laser at wavelength of 266 nm and the laser output power was 20 mW. The laser pulse width was 200 fs and the repetition rate was 76 MHz. The luminescence spectrum was measured by a 0.5 m monochromator and detected by a photomultiplier tube. The cathodoluminescence (CL) measurements were carried out at 300 K by using a MonoCL system installed on a field emission scanning electron microscope (SEM) with beam energies of 5–20 keV. The threading dislocations and the sharpness of the AlGaN/GaN interfaces were studied by transmission electron microscope (TEM). The dislocation density of the sample surface with an area of 20 µm × 26 µm was analyzed after the 5-minute etching in the KOH solution with 0.005M at 80°C.

Fig. 2(a) and (b) show the HRXRD ω/2θ diffraction pattern and the RSM of the as-grown AlGaN/GaN MQWs sample. In Fig. 2(a), the HRXRD diffraction pattern shows two periodical structures: one can be attributed to the AlGaN/GaN MQWs; another can be attributed to the AlN/GaN SLs in the AlGaN barriers. The third order satellite peak of the diffraction pattern for AlGaN/GaN MQWs can be clearly observed, suggesting the high crystalline quality of AlGaN/GaN MQWs and AlN/GaN SLs. The thickness of AlN and GaN in the barrier and the GaN wells can be fitted to be about 0.42, 0.77, and 2.9 nm, respectively. The average Al content of AlGaN barrier is also

estimated to be about 0.29. From the RSM data of AlGaN/GaN MQWs obtained from $(10\bar{1}5)$ diffraction shown in Fig. 2(b), the spread of RSM intensity for the AlGaN/GaN MQWs was relatively narrow indicating AlGaN epilayers exhibited relatively small distribution of crystal orientation [1]. In addition, the reciprocal lattice points of AlGaN and GaN were lined up at the same Q_x position (red solid line) indicating the AlGaN and GaN had same lattice constant. According the earlier report [2], the degree of lattice relaxations can be estimated from the equation of $\varepsilon_{xx}= q_x^{GaN} / q_x^{MQWs} -1$, where the q_x^{GaN} and q_x^{MQWs} are the x position of GaN layer and AlGaN layer, respectively. We obtained an estimated degree of lattice relaxation to be only 3.9×10^{-6}, indicating the AlGaN epilayer is fully strained and pseudomorphic to the underlying GaN layer.

As shown in Fig. 3(a), the surface morphology of the top layer was observed by atomic force microscope and no cracks were found. A very small RMS value of the surface roughness of 0.35 nm was achieved. To carefully investigate the threading dislocation within our sample, both cross-sectional and plane-view TEM images were taken. Fig. 3(b) shows the cross-sectional TEM image of the sample with the white dash lines indicating the top and bottom GaN epilayer regions. It is clear that few dislocations are observable and only one dislocation passes through the GaN epilayer into AlGaN/GaN MQWs. The dislocation density (DD) at the bottom GaN layer is about 3.5×10^{8} cm^{-2} and slightly reduces to 1.4×10^{8} cm^{-2} at the top GaN layer. However, the DD in the AlGaN/GaN MQWs region is only 2.5×10^{7} cm^{-2}. Fig. 3(c) shows the plane-view bright-field TEM image from the top surface. The dislocation density was estimated to be about 3.2×10^{7} cm^{-2}. Meanwhile, we also estimate the dislocation density in this AlGaN/GaN MQWs sample by evaluating the etch-pit density (EPD) of the KOH etched sample. We obtain an estimated EPD value of about 3.3×10^{7} cm^{-2}, which is similar to the above estimated plain-view DD value. These estimated DD values of our sample are nearly two orders of magnitude lower than that of AlGaN films, which were not grown by ALD, reported recently [2]. From the enlarged TEM image shown in the inset of Fig. 3 (d), it can be clearly observed that the QWs and SLs exhibited sharp interfaces with good periodicity, showing that the high quality SLs and MQWs were formed by the ALD technique. The image also show that the AlGaN barrier consisted of six pairs AlN/GaN SLs with AlN thickness of 0.43 nm and GaN thickness of 0.77 nm, respectively forming a AlGaN barrier with thickness of 7.2 nm, and the GaN well had a thickness of 3 nm, which are in good agreement with the result estimated from HRXRD data.

Interestingly, a bending of threading dislocations at the boundary of MQWs without extending into the top surface was commonly observed in this sample as shown in Fig. 3(d). Previous it was reported [3] that the strain in the epi-layer could exert a net force on the dislocation to be bended or terminated at the strained epilayer edge without threading through the epilayer to the top surface. Since our RSM result demonstrated that the AlGaN epilayer is fully strained, it suggested that the large strain in the ALD grown AlGaN barrier with AlN/GaN SLs could effectively bend and suppress the threading dislocations, thus reducing the defects in MQW and improving the surface morphology of the sample.

Fig. 4 shows the PL spectra of the as-grown sample. The emission peak energy at 3.60 eV and 3.71 eV was observed at room temperature and 13K, respectively. The full

width at half maximum (FWHM) of PL spectra is about 80 meV at room temperature and reduces to only 47 meV at 13 K, which are smaller than the previous report by a factor of 2-3 [4], indicating that the crystal quality of AlGaN/GaN MQWs has been improved by using ALD AlGaN barrier. Our PL data analysis confirmed that the two dominant emission peak energy of 3.60 and 3.71 eV at room temperature and 13K, respectively, was emitted from GaN well. In addition, the emission peak energy at 3.62 eV can be clearly observed at 13K. According to previous report, the emission peak energy of 3.62 eV could be attributed to the LO phonon [5]. Additionally, the inset of Fig. 4 shows the CL image of the sample which has near uniform brightness with few dark spots. It was well-known that the dark spots in CL image were related to non-radiative centers in the defects of epilayers. Therefore the CL image data again suggest our sample has relatively low dislocation density and superior crystalline quality.

2.4 Fabrication of GaN-based LED with ALD grown MQW

The high dislocation density led to the poor performance of UV-LED because the threading dislocation density act non-radiative centers and reduce the radiative recombination efficiency. In our early reports, the strain atomic layer is very useful for suppression of dislocation in lattice mismatch epilayers. Therefore, low dislocation density is a key issue for high efficient UV light emitting devices. Based on the realization of high efficient UV light emitting devices, we will further fabricate UV LEDs with inserting ALD-AlGaN/GaN strain layer. The proposed UV -LEDs with ALD-AlGaN/GaN strain layer and conventional UV LEDs were show in Fig 5.

2.5 Performance of LED with ALD grown MQW

Figure 6 shows relative PL quantum efficiency for both samples at 15 and 300 K. Curves are normalized by the peak value at 15 K for both samples, and the constant *C* in Eq. (1) is canceled out with this normalization [6]. As can be seen, the efficiency is strongly dependent on excitation power density. The results show that the IQE of sample with ALD layers was estimated to be 70.2 %, which is higher than 5% IQE of sample without ALD layers, suggesting that the sample with ALD grown AlGaN/GaN superlattice of good crystal quality and slighting potential fluctuation was grown.

$$\eta_{PL} = C\frac{I_{PL}/E_{PL}}{I_{EX}/E_{EX}} \tag{1}$$

3 Summary

In summary, we have grown low dislocation and high crystalline quality AlGaN/GaN MQWs on sapphire substrate by using the ALD grown AlGaN barrier consisted of AlN/GaN SLs. The AFM data show smooth surface morphology with a small surface roughness RMS value of about 0.35 nm and no surface cracks. The TEM and HRXRD measurements show that the grown sample has sharp interfaces between SLs layers and QWs with good periodicity. The sample has near uniform CL image intensity at room temperature and narrow PL emission peak. The sample has a low dislocation density of about 3.3×10^{7} cm^{-2}. These results indicate that the AlGaN/GaN MQWs grown by the ALD technique is a viable method for growth of a device-quality AlGaN/GaN MQWs structure for various optical devices.

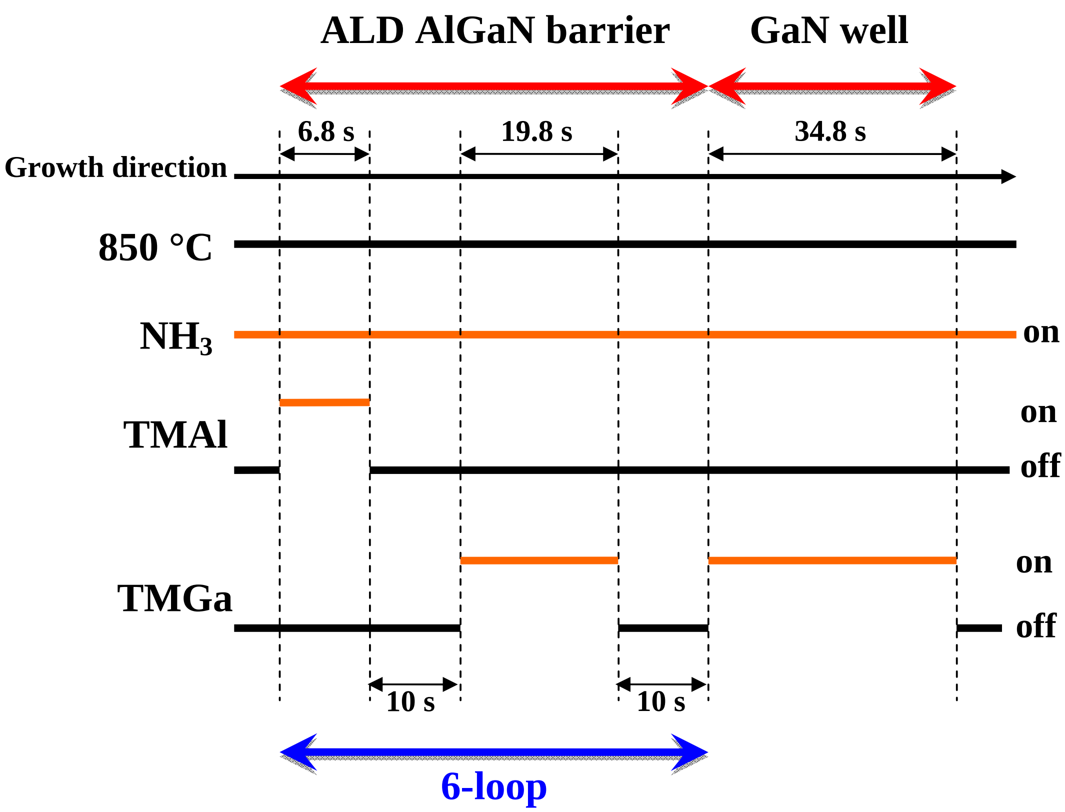


Fig. 1 Growth procedure of AlGaN barrier and GaN well layers.

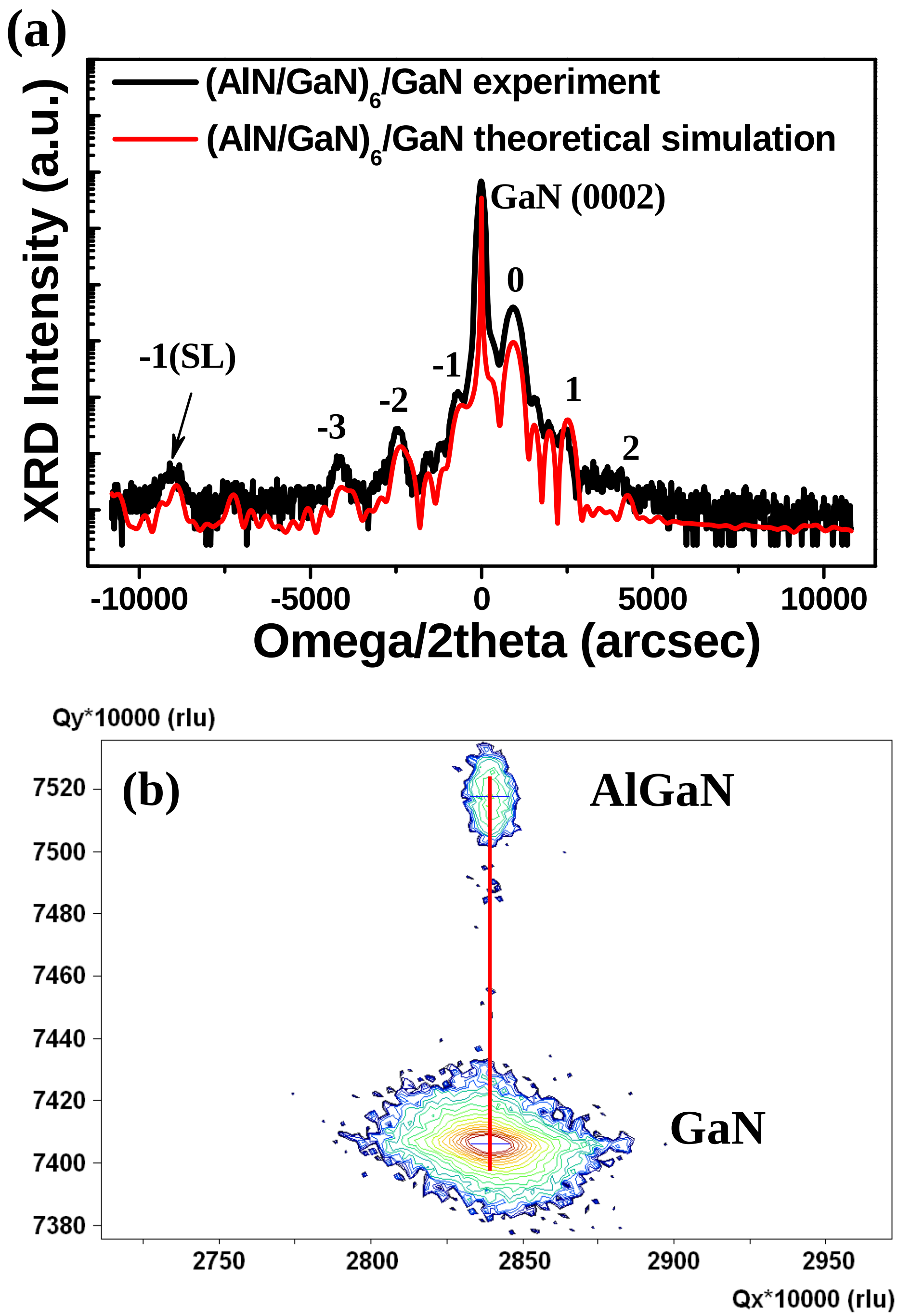


Fig. 2(a) high-resolution x-ray diffraction pattern at (0002) plane for the AlGaN/GaN MQWs sample, (b) RSM of the sample obtained from $(10\bar{1}5)$ diffraction.

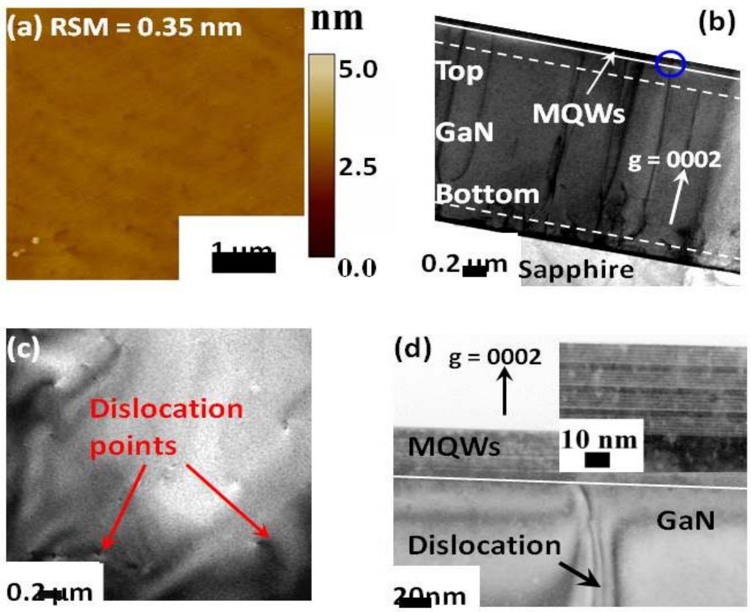


Fig. 3(a) Surface morphology of the grown AlGaN/GaN MQWs sample scanned by AFM; (b) cross-sectional TEM image and (c) plane-view TEM image of the AlGaN/GaN MQWs sample ; (d) enlarged cross-sectional TEM images of the sample

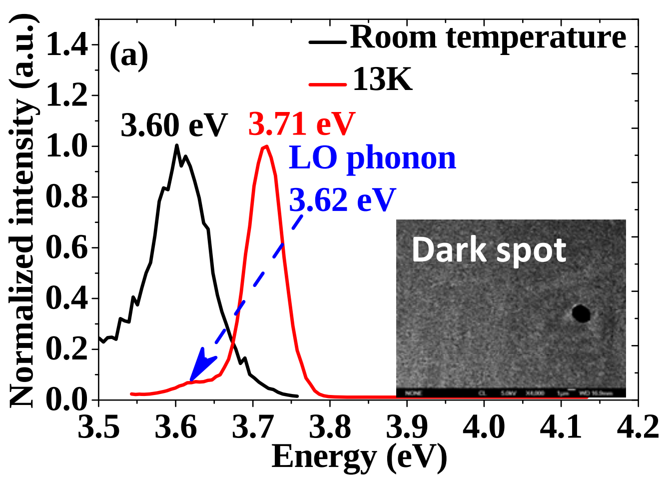
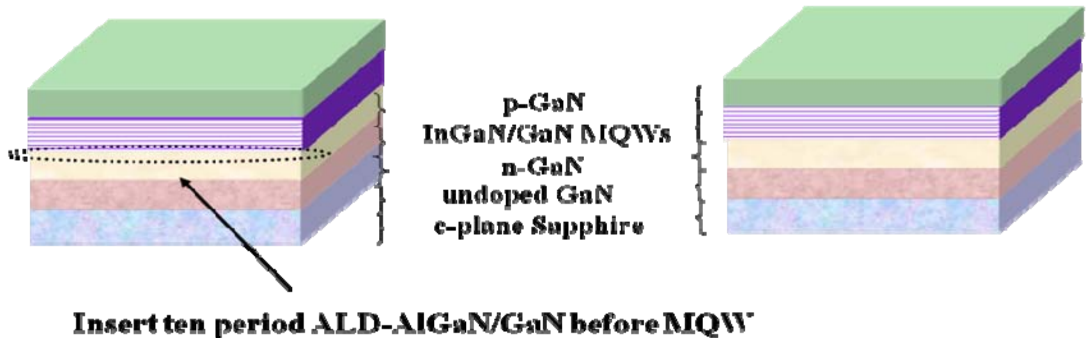


Fig. 4 The 13K and room temperature PL spectra of the AlGaN/GaN MQWs sample. Inset shows CL image taken at E = 3.71 eV.



(a) LED with ALD Structure (b) Conventional LED

Fig. 5 Schematic drawing of (a) LED with ALD Structure (b) Conventional LED

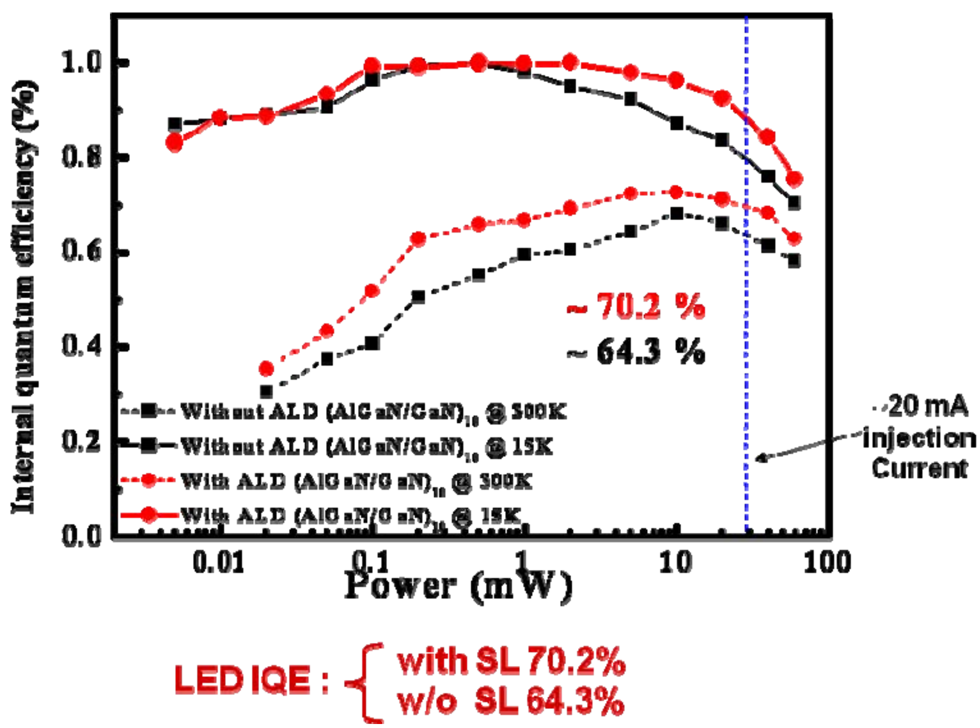


Fig.6. Internal quantum efficiency as a function of different excitation conditions at 15 K and 300 K.

4 Publications

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